ELSEVIER

Chemical Engineering Journal 106 (2005) 91–96

Chemical Engineering Journal
www.elsevier.com/locate/cej

A two-zone fluidized bed reactor for catalytic propane dehydrogenation

J. Gascón, C. Téllez, J. Herguido, M. Menéndez*

Department of Chemical and Environmental Engineering, University of Zaragoza, 50009 Zaragoza, Spain

Received 28 September 2004; received in revised form 10 November 2004; accepted 13 November 2004

Abstract

A new reactor technology is employed for propane dehydrogenation over a Cr_2O_3/Al_2O_3 catalyst. This reactor allows the continuous regeneration of the catalyst, but avoids the transfer of large amounts of solid between two reactors, since one single vessel is employed. The experimental work was carried out in a bench scale reactor using two configurations: (a) a two-zone fluidized bed reactor (TZFBR), where propane and oxygen are fed at different levels, providing separated zones for the reaction and catalyst regeneration; (b) an internal circulating fluidized bed reactor (ICFBR), where the addition of an axial dividing slab allows the partition of the vessel, giving two beds connected at the top and bottom and enabling better catalyst circulation. The effects of the main operating variables were studied: bed temperature, gas velocity, oxygen flow rate fed to the reactor, relative length between the oxidizing and reacting zones and the *W*/*F* ratio. Under suitable conditions, steady-state operation with propene yields as high as 30% can be achieved, with small requirements of oxygen to continuously regenerate the catalyst.

Keywords: Propane dehydrogenation; Cr_2O_3/Al_2O_3 catalysts; Catalyst deactivation; Circulating fluidized bed

1. Introduction

The international chemical market has demonstrated during the last decade a great interest in processes involving light olefins production because of its interest as starting materials in some of the most important polymers, oxygenated compounds and synthetic rubbers manufacture, propane is currently produced as a co-product of ethylene. Recent reports [1] indicate that the growth rate of propene demand will surpass that of ethylene until the year 2005, in spite of the fact that ethylene consumption is anticipated to double by 2015. Several schemes have been proposed for propene industrial production (e.g. oxidative dehydrogenation [2–4], metathesis [5]) but nowadays, catalytic dehydrogenation is the most feasible for propane upgrading on a commercial scale.

Propane dehydrogenation is an equilibrium limited and a highly endothermic reaction that is generally carried out at 525–625 °C and atmospheric pressure using platinum or chromium catalysts; those catalyst are not full selective, and dehydrogenation is accompanied by cracking and coking reactions.

Catalyst deactivation by coking is the common problem of the non-oxidative dehydrogenation processes. To remove these coke deposits from the catalyst surface, combustion with oxygen–diluent mixtures is often carried out off-line, either in separate or in the same reactor, after purging the flammable hydrocarbon gases. In any case, the downtime for regeneration represents a significant economic penalty, which provides the driving force for processes where the catalyst is continuously regenerated. Commercial processes for light olefins dehydrogenation based on this continuous regeneration can be found, such as the propane fluidized bed dehydrogenation (FBD-3) [6,7] from Snamprogetty, in which separate reactors are used for reaction and regeneration and large amounts of catalyst must be transferred between both vessels.

Another problem associated with all the industrial dehydrogenation reactors is how to supply the huge quantity of heat needed by the reaction, maintaining a careful control of the temperature to minimize the formation of other products

---

* Corresponding author. Tel.: +34 976 761152; fax: +34 976 762142.
E-mail address: qtmiguel@posta.unizar.es (M. Menéndez).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.11.005

Nomenclature

F	molar flow (mol/min)
h	bed height (cm)
h_c	height of the hydrocarbon feed point (cm)
ICFBR	internal circulating fluidized bed reactor
TZFBR	two-zone fluidized bed reactor
u	gas velocity (cm (STP)/min)
u_{mf}	minimum fluidization velocity (cm (STP)/min)
u_r	relative gas velocity (u/u_{mf})
W	amount of catalyst in the reactor (g)
W_r	amount of catalyst in the reacting zone (g)

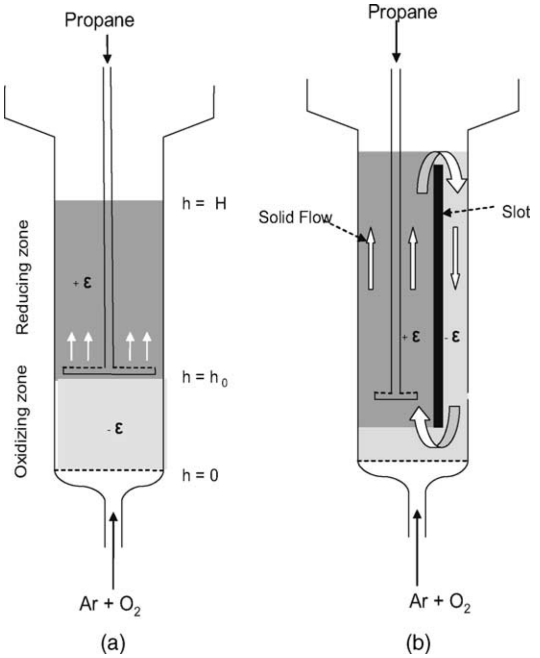

Fig. 1. Scheme of the configurations used in this work: (a) TZFBR; (b) ICFBR.

(cracking) in order to maximize the yield to the desired product. In some processes, the heat is supplied in part by the sensible heat stored in the catalyst bed during the regeneration step, and in other cases, additional heat is provided by direct fuel combustion.

A variety of technologies are available commercially for propane dehydrogenation [8], such as the Oleflex Process, developed by UOP, the Houdry Catofin Process (Air Products), the Phillips STAR Process (Phillips Petroleum), the Linde Process or the FBD-3 explained before. The great majority operates in a cyclic way with fixed bed reactors and propane is co-fed with hydrogen to decrease coke formation. Overall propene selectivities of 85–90% are claimed.

Although propane dehydrogenation has been widely studied and it is a well-established process, increases in the yield-selectivity relation, a better heat recover and other operational advantages are still possible. To this end, reactors have been tested for the reactions, such as the rotating monolith reactor proposed by Stitt et al. [9] or membrane reactors to displace the equilibrium [10].

During last years, our group has studied [11–16] a new concept of fluidized bed reactors. It aims to exploit the fast solid mixing characteristic of fluidized beds in order to obtain a controlled solid flow between two-zones; as a result, the catalyst regeneration can be performed in the same reactor where the desired reaction is being carried out. Most of the works developed in this reactor have been partial oxidation processes, such as oxidative coupling of methane [11], oxidative dehydrogenation of butane [12–14] and partial oxidation of butane to maleic anhydride [15]. Also, butane catalytic dehydrogenation at lab scale [16], as an example of non-oxidative reaction, has been previously studied at laboratory scale. It was demonstrated that stable operation can be achieved in the non-oxidative dehydrogenation, besides yields comparable to the maximum initial yields reported in works where conventional dehydrogenation takes place simultaneously with net coke formation and catalyst deactivation have been obtained. A similar system where oxygen and hydrocarbon are fed separately to a fluidized bed was first described in an old patent [17], but no details of the system were given. Several other systems have been proposed to transfer solid between adjacent fluid beds or parts of a bed. Apart from the CFBR [18], which has been widely studied, given its use for the FCC process and for coal combustion, several other systems have been described in the literature [19–21]. All of them have the same characteristic of transporting the solid between different zones of a single vessel, usually with the aim of employing each zone for a different step of a process.

In this work, propane dehydrogenation over a Cr_2O_3 catalyst has been studied in a bench scale plant, using a two-zone fluidized bed reactor (TZFBR) configuration. The TZFBR (Fig. 1a) uses segregated feeds for the oxidant and the hydrocarbon in a single vessel. This allows coke combustion to take place in the oxidizing zone and the hydrocarbon reactions to the desired product in the reacting zone while the catalyst circulates between both zones due to fast solid mixing characteristic of fluidized beds. The other configuration used occasionally is the internal circulation fluidized bed reactor (ICFBR, Fig. 1b) where an axial dividing slab allowed the partition of the column in two beds connected from the bottom and the top. Propane is fed in one of the partition and the oxygen containing mixture was fed to the bottom of the reactor. Since both beds have a different gas velocity, the different porosity results in a different pressure drop (smaller in the bed with larger porosity) and the pressure difference that appears at the void space (at the end of the divider) connecting both beds causes the solid circulation between the oxidizing and the reacting zones. In order to better understand the reaction, a previous kinetic model for chemical reaction [22], coke formation and effect of coke over catalyst deactivation has been developed under transient conditions.

2. Experimental

A scheme of the reaction system employed is shown in Fig. 1. The reactor was a 6 cm diameter, 100 cm long stainless steel tube, and two configurations have been proved; in the first one, named TZFBR (Fig. 1a) propane was fed in the middle height of the bed (h_h), and an O_2–Ar mixture was fed in the bottom of the reactor. In the alternative configuration, named ICFBR (Fig. 1b), an axial dividing slab of 0.6 m long in the reactor allowed the partition of the column with a thin plate in two regions of 1/3 and 2/3 of the total cross sectional area of the column, oxygen and propane were fed in some of the both reactor partitions. As it has been explained previously, the porosity difference produces the catalyst circulation between both reactor regions.

In all the experiments performed, a commercial Cr_2O_3/Al_2O_3 catalyst, supplied by Nikki Chemical (N401 AG), was used. Before the reaction, the catalyst was ground and sieved to a particle size of 160–250 μm, calcined in air at 650 °C, and treated under seven reaction-regeneration cycles for 30 min each at 600 °C to obtain an aged and stable catalyst [23,24]. All the streams were mass flow controlled (Brooks). The total feed flow ($Ar + O_2$ and C_3H_8) was varied between 2700 and 3600 cm^3 (STP)/min and corresponds to three and four times the minimum fluidization conditions. Propane feed in the experiments corresponds to around 50% of the total feed. A mobile axial stainless steel probe was used to introduce the propane at different reactor heights. The mass of catalyst in the bed was varied between 400 g and 800 g. The temperature was varied from 525 °C to 575 °C. By using a mobile thermocouple, axial temperature profiles have been determined in most of the experiments, obtaining a near constant profile in all cases. Typically, the temperature difference between the top and the bottom of the bed in the TZFBR was smaller than 10 °C.

The exit gases were analyzed by online gas chromatography (CE Instruments model GC-8000TOP, with TCD and FID detectors, using Chromosorb PAW 23% SP-170080/100 and Molecular sieve 10 A 80/100 columns). Carbon balances were always better than ±5% and usually better than ±3% for the steady-state experiments reported in this work.

Also, a mobile axial stainless steel probe was used to take samples of the catalyst to analyze the coke content in the catalyst along the bed. The combustion of the samples was carried out on a 6 mm internal diameter tubular quartz reactor. The exit gases were collected in bag and analyzed by GC.

The main reactor-related variables studied were bed temperature (T), oxygen flow rate fed in the reactor, the relative height of the oxidizing and reacting zones and the relation between catalyst mass in the reacting zone and propane feed (W_r/F).

3. Results and discussion

Fluidization conditions of the used catalyst were determined in a previous stage by performing different experiments in the absence of reaction. Particle sizes below 150 μm can produce cohesive behavior, with formation of channels through the bed, while a good fluidization was found with the size range between 160 μm and 250 μm. Using Ar at 550 °C, a minimum fluidization velocity (u_{mf}) of 30.6 cm (STP)/min has been calculated from the bed pressure drop versus flow rate curve.

Fig. 2 shows the evolution of propane conversion and propene yield as a function of time for the TZFBR, transient behavior was observed for about 30 min, after which the conversion and selectivities were stable. This is due to the stabilization of the coke content of the catalyst along the reactor for a given set of conditions. That means that constant exit flow rates are achieved after an equilibrium is achieved between coke formation in the reacting zone and coke burning in the oxidizing zone. Therefore, CO_x's appear as a product of coke burning in the oxidizing zone, but always in a very low concentration (less than a 4%). The amount of CO_x formed agrees well with the oxygen fed, and therefore the steam reforming of propane is not significant. Also cracking products, mainly methane and ethylene, are detected. The same stability behavior was found for the ICFBR configuration. In packed bed reactor (PBR) without feeding oxygen, propane conversion and yield to propene (Fig. 2) decreases strongly with time due to deactivation by coke deposition. After that, all the results reported correspond to the steady-state, obtained after 4 h on reaction. Regarding the stability of the catalysts, after 800 h under different operation conditions, the conversion and selectivities measured for the used catalyst were within 5% deviation from the initial values.

Fig. 3 shows the effect of the amount of O_2 fed in TZFBR configuration. These experiments were carried out with a constant input of argon and propane, while the flow of oxygen

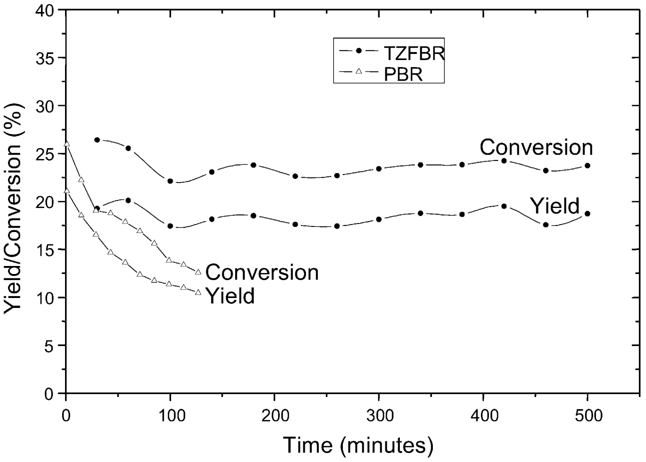

Fig. 2. Evolution of propane conversion and propene yield with time. $T = 550\,^\circ C$; $W/F = 100$ g h/mol; $Q_{Ar} = 20$ cm^3 (STP)/s; $Q_{O_2} = 2$ cm^3 (STP)/s; $Q_{C_3H_8} = 26$ cm^3 (STP)/s, $h_h = 8$ cm; $H = 20$ cm.

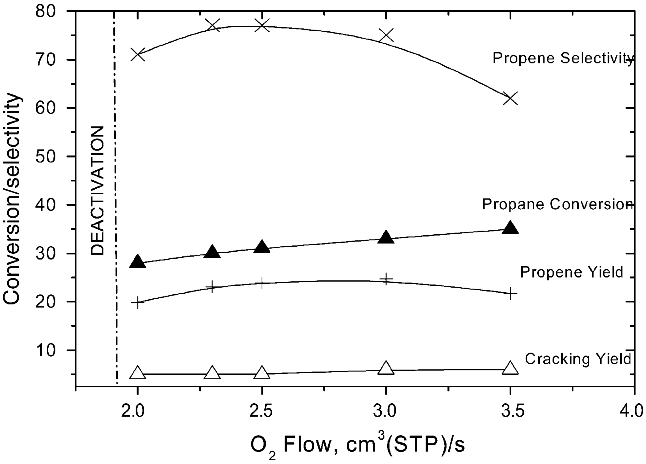

Fig. 3. Influence of the O_2 flow upon propane conversion, propene selectivity and cracking yield. Configuration: TZFBR; $T = 550\,°C$; $W/F = 150$ g h/mol; $Q_{Ar} = 24\,cm^3$ (STP)/s; $Q_{C_3H_8} = 26\,cm^3$ (STP)/s. $h_h/H = 0.5$.

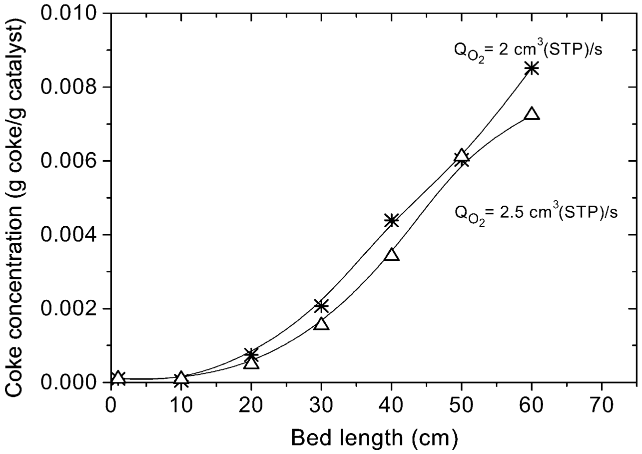

Fig. 4. Coke concentration along the catalyst bed for two different O_2 flow rates fed in the reactor, operation conditions same as Fig. 3.

was varied. It can be seen that propane conversion increases with oxygen flow, probably due to the higher quantity of coke burning and as a consequence of a higher catalyst activity. Between 2 cm^3 (STP)/s and 3 cm^3 (STP)/s, the propene selectivity is nearly constant, but quantities of oxygen greater than a limit (ca. 3 cm^3 (STP)/s) produce a decrease in propene selectivity, while propane conversion continue increasing. These results could be explained because if there is more oxygen than the amount necessary to burn the coke formed in the reacting zone new reactions could take place. Cr_2O_3/Al_2O_3 catalyst is able to promote combustion [25] then, the hydrocarbon will react with the remaining oxygen to produce CO_x's and propene selectivity will decrease. These results are in agreement with previous work in butane dehydrogenation [16]. Otherwise, an excess of oxygen could oxidize Cr^{3+} to Cr^{6+} which is also active in CO_x formation. No results are given with oxygen flow less than 2 ml/s because in those experiments the catalyst becomes deactivated without achieving a steady-state. The flow rate of oxygen fed is obviously important in the reactor configuration used in this work for the propane dehydrogenation. It must be able to achieve equilibrium between the coke formed in the reacting zone and the coke burning in the oxidized zone, and at the same time avoiding propane and oxygen mixing, which produces CO_x formation.

The coke content in catalyst along the bed has been analyzed using a solid probe to extract catalyst samples at several axial positions. Fig. 4 shows the results obtained for coke content in catalyst along the bed for two different flow rates of oxygen fed to the reactor. The amount of coke increases along the bed, more quickly over the point where propane is fed in the reactor ($h_h = 30$ cm). As it could be expected, a higher oxygen flow rate decreases the amount of coke, which agrees with the greater conversion and selectivity obtained (Fig. 3).

The effect of W_r/F ratio on the propane yield is shown in Fig. 5. These experiments were carried out by varying the catalyst load in the bed with a height ratio of the reacting zone/oxidizing zone equal to 1($h_h/H = 1/2$). As was explained before, an optimum of oxygen flow rate is found for each W_r/F ratio. It can be observed that the propene yield in the optimum increases with the W_r/F ratio because propane conversion increases largely whereas propene selectivity decreases slightly (not showed). The optimum of oxygen flowrate appears in a narrow range, around 2–3 cm^3 (STP)/min due probably to that the ratio oxidizing zone/reacting zone is the same and the larger the amount of catalyst, the higher the rate of coke formation, which implies also the need to increase the oxidizing zone to burn the formed coke.

Fig. 6 shows the propane conversion and the selectivity to propene for the same catalyst weight in the reactor (W) but for different propane entry points (h_h), i.e. for the same total height of the bed (H) but different relation between the height

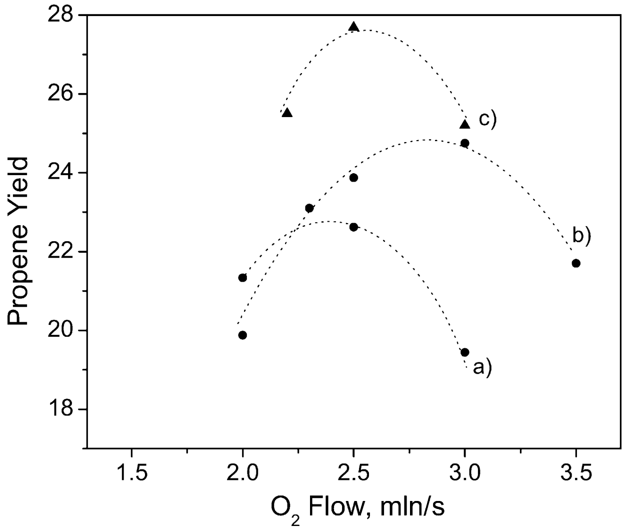

Fig. 5. Influence of W/F upon propene yield: (a) $W/F = 125$ g h/mol, TZFBR. (b) $W/F = 150$ g h/mol, TZFBR. (c) $W/F = 200$ g h/mol, TZFBR. Other conditions: $T = 550\,°C$, $Q_{Ar} = 24\,cm^3$ (STP)/s, $Q_{C_3H_8} = 26\,cm^3$ (STP)/s.

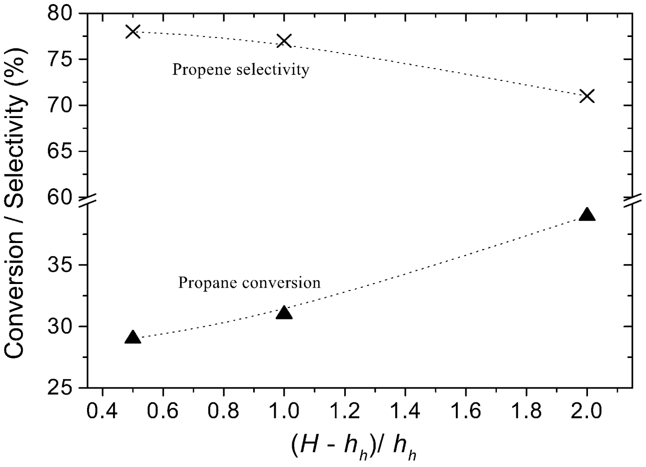

Fig. 6. Influence of relation between the length of the reducing and the oxidizing zones using the same amount of catalyst in the bed. Configuration: TZFBR, $T = 550\,°C$, $Q_{Ar} = 24\,cm^3$ (STP)/s, $Q_{C_3H_8} = 26\,cm^3$ (STP)/s, $Q_O = 2.5\,cm^3$ (STP)/s, weight of catalyst: 800 g.

of the reducing and the oxidizing zones (then different W_r/F ratio). The feed flows of oxygen, propane and argon fed in the reactor were the same for all cases. It is clear from Fig. 6 that more catalyst in contact with propane produces more conversion but decreases propene selectivity. These results can be explained with the help of a previous kinetic study [22] since in the experiments with a larger reacting zone, the catalyst reaches a higher coke content which affects the dehydrogenation reaction, but not the cracking. Relations between length zones greater than two do not allow the catalyst to be regenerated with the oxygen flow fed in this set of experiments due to the higher coke formation and smaller oxidizing zone.

The effect of the temperature upon the conversion and selectivities is presented in Fig. 7. These experiments were carried out with a constant input of argon and propane, while the flow of oxygen was varied in order to achieve an optimum steady-state at each temperature (525 °C, 550 °C and 575 °C). As is expected from the kinetic model on coke formation previously developed [22], around five times more coke is formed at the highest temperature studied (575 °C) than at the lowest (525 °C), producing a great oxygen demand to obtain the steady-state. As the temperature was raised in the 525–575 °C interval, the propane conversion increased and the propene selectivity decreased. Conversion increases quickly with temperature because dehydrogenation and cracking are both very endothermic reactions and, as a result, a small rise in temperature produces a large increase in conversion. Also, the yield to CO_x at the highest temperature is much greater than at the lowest temperature due to the larger oxygen flow fed to burn the coke formed. On the other hand, selectivity to propene decreases with temperature as could be expected due the lower activation energy for propane dehydrogenation (8.5 kcal/mol) than for cracking reaction (73.8 kcal/mol) [22].

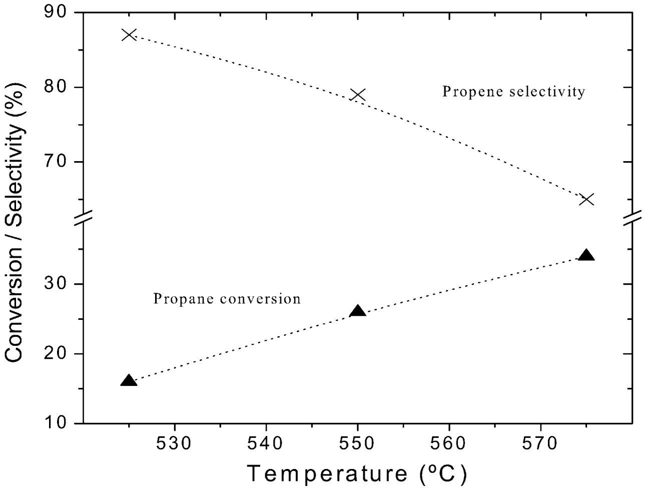

Fig. 7. Effect of temperature upon propane conversion and propene selectivity. Configuration: TZFBR, $W/F = 125$ g h/mol, $Q_{Ar} = 24\,cm^3$ (STP)/s, $Q_{C_3H_8} = 26\,cm^3$ (STP)/s, $h_h/H = 0.5$.

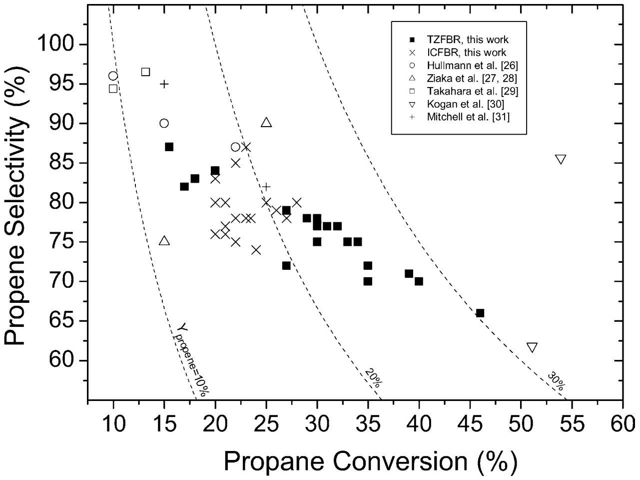

Fig. 8. Conversion vs. selectivity for the experiments performed during this work in TZFBR and ICFBR configurations and comparison with results in the literature. Diverse operating conditions.

In order to compare with the results in the TZFBR, some experiments in the ICFBR system have also been performed. Fig. 8 shows the selectivity versus conversion for the experiments obtained in both reactor configurations at several operating conditions. For both reactors, the optimum conditions seem to have a linear relation; for a given conversion there is nearly constant selectivity independently on the operating conditions. The trend observed in this figure is that the TZFBR allows higher conversion, but with a penalty on selectivity. Changes in conversion with the operating conditions are less pronounced in the ICFBR than in the TZFBR, at least under the restrictions existing in our experimental system. Otherwise it was found that the selectivity for a given conversion was more variable in the ICFBR than in the TZFBR. The explanation of these phenomena is not clear, but probably is related with the different solid flow patterns in both reactors. A mathematical model is currently being developed to gain a better understanding of the complex relationship between the solid flow, the reaction and deactivation kinetics and the reactor performance. Fig. 8 also shows the best results obtained in other works using different catalysts for propane dehydrogenation in several experimental systems: Hullmann et al. [26] used a platinum silicon nitride catalyst in a tubular fixed bed reactor, propane was co-fed with H_2; results presented from Ziaka et al. [27,28] correspond to a catalytic membrane reactor with a Pt/Al_2O_3 catalyst. Takahara et al. [29] developed their work using several Cr_2O_3 catalysts in fixed bed reactors. Kogan et al. [30] used a modified Pt/Al_2O_3 catalyst in a hydrogen–steam environment, while Mitchell et al. [31] employed a molybdenum hydrocalcite catalyst in a fixed bed reactor. Only those results obtained with a high dilution of propane [30] or with a membrane reactor [27,28] allow achieving higher selectivity for a given conversion, at least for conversions over 15%. However, the use of high dilution implies further costs for the product recovery, and the catalyst is quickly deactivated by coke in membrane reactors due to the low partial pressure of hydrogen.

4. Conclusions

This work demonstrated that TZFBR and ICFBR reactors can be used in the catalytic propane dehydrogenation to obtain steady-state operation. Yields of propene up to 30% have been achieved, which are comparable to the highest yields reported in conventional reactors, where the coke formation causes the catalyst deactivation and a decrease of conversion with the time on stream. In these new reactor technology, the operation conditions (bed temperature, gas velocity, the oxygen fed in the reactor, the relative length of the oxidizing and reacting zones, and W_r/F ratio) play key role in the reactor performance, because stable operation is only achieved when the rates of coke formation in the reducing zone and of coke burning in the oxidizing zone are equal. The optimum experimental conditions have been investigated and it was found that the flowrate of oxygen fed is related with the coke formed in the reacting zone.

Thus, the TZFBR and ICFBR have other advantages over conventional reactors: (a) No hydrogen is needed to reduce coke formation, in difference to that is needed in many of the available commercial processes for olefin dehydrogenation. (b) The coke formed using this system becomes an important source of energy because its burning produces a part of the energy necessary for the dehydrogenation reaction. (c) Reaction and catalyst regeneration take place in the same vessel. (d) Oxygen and hydrocarbon are fed at different levels avoiding flammable mixture.

Acknowledgement

The authors thank DGI (Spain) for financial support in the project PPQ-2001-2519-CO2-01.

References

[1] J. Cosyns, J. Chodorge, D. Commereuc, B. Torck, Hydrocarbon Process. (March 1998).
[2] H.H. Kung, Adv. Catal. 40 (1994) 1.
[3] E.A. Memedov, V. Cortés-Corberán, Appl. Catal. 127 (1995) 1.
[4] T. Blasco, J.M. López Nieto, Appl. Catal. 157 (1997) 117.
[5] P. Amigues, Y. Chauvin, D. Commereuc, J. Mol. Catal. 65 (1991) 39.
[6] D. Sanfilippo, F. Buomo, G. Fusco, Chem. Eng. Sci. 47 (1992) 2313.
[7] I. Miracca, L. Piovesan, Catal. Today 52 (1999) 259.
[8] P. Eisele, R. Killpack, Ullmann's Encyclopedia of Industrial Chemistry, sixth ed., Villey-CCH, Weinheim, 1998.
[9] E.H. Stitt, S.D. Jackson, D.G. Shipley, F. King, Catal. Today 69 (2001) 217.
[10] J. Coronas, J. Santamaría, Catal. Today 51 (1999) 377.
[11] R. Ramos, J. Herguido, M. Menéndez, J. Santamaría, J. Catal. Lett. 50 (1998) 25.
[12] J. Soler, J.M. López Nieto, J. Herguido, M. Menéndez, J. Santamaría, Ind. Eng. Chem. Res. 38 (1999) 90.
[13] M.L. Pacheco, J. Soler, A. Dejoz, J.M. López Nieto, J. Herguido, M. Menéndez, J. Santamaría, Catal. Today 61 (2000) 101.
[14] J. Soler, C. Téllez, J. Herguido, M. Menéndez, J. Santamaría, Powder Technol. 120 (2001) 88.
[15] O. Rubio, R. Mallada, J. Herguido, M. Menéndez, Ind. Eng. Chem. Res. 41 (2002) 5181.
[16] C. Callejas, J. Soler, J. Herguido, M. Menéndez, J. Santamaría, Stud. Surf. Sci. Catal. 130 (2000) 2717.
[17] P. D. Montgomery, R. N. Moore, W.R. Knox US, Patent 3,965,206 (June 1976).
[18] D. Kunii, O. Levenspiel, Chem. Eng. Sci. 52 (1997) 2471.
[19] M. Kuramoto, T. Furusawa, D. Kunii, Powder Technol. 44 (1985) 77.
[20] R. Korbee, J.C. Schouten, C.M. Van der Bleek, AIChE Symp. Ser. 281 (1991) 70.
[21] A. Reichhold, H. Hofbauer, Chem. Eng. Process. 34 (1995) 521.
[22] J. Gascón, C. Téllez, J. Herguido, M. Menéndez, Appl. Catal. A Gen. 248 (2003) 105.
[23] J.A. Peña, A. Monzón, J. Santamaría, Appl. Catal. Part A: Gen. 101 (1993) 185.
[24] J.A. Peña, A. Monzón, J. Santamaría, J. Catal. 142 (1993) 59.
[25] C. Royo, M. Menéndez, J. Santamaría, React. Kinet. Catal. Lett. 44 (1991) 445.
[26] D. Hullmann, G. Wendt, U. Singliar, G. Ziegenbalg, Appl. Catal. Part A: Gen. 225 (2002) 261.
[27] Z.D. Ziaka, R.G. Minet, T.T. Tsotsis, J. Membr. Sci. 77 (1993) 221.
[28] Z.D. Ziaka, R.G. Minet, T.T. Tsotsis, AIChE J. 39 (1993) 526.
[29] I. Takahara, W.-C. Chang, N. Mimura, M. Saito, Catal. Today 45 (1998) 55.
[30] S.B. Kogan, H. Schramm, M. Herskowitz, Appl. Catal. Part A: Gen. 208 (2001) 185.
[31] P.C.H. Mitchell, S.A. Wass, Appl. Catal. Part A: Gen. 225 (2002) 153.